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Amorphous Phase Formation in the Zirconium-Poor Corner of (Fe,Co,Ni)-Zr systems*

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Synopsis

The formation of amorphous phase was found in the limited region around 10 at% zirconium in (Fe,Co,Ni)-Zr systems. Their Vickers hardness and fracture strength were of the order of about 550-700 DPN and 1700-2100 MPa, respectively. They also were crystallized on heating at about 340-500°C and remained ductile until the crystallization temperature.

I. Introduction

Amorphous alloys have been found in a large number of alloy systems by means of melt-quenching. These alloy systems can be classified generally into two categories; namely, the metal-metalloid type and the metal-metal type. Most of amorphous alloys found so far belong to the former type and contain about 20 at% of various combination of boron, carbon, silicon and germanium. On the other hand, the amorphous alloys belonging to the later type are limited to several alloy systems consisting of early transition metal and late transition metal such as Cu-Zr(1,2), Ni-Zr(1), Co-Zr(1) and Ni-Nb(3). Amongst these amorphous alloys, the former type alloys occupy a prominent place because of their potential for industrial applications in the fields of magnetic materials. However, the later type alloys have no interest in industrial point of view due to containing less amount of ferro-magnetic elements such as iron and cobalt.

Recently Buschow and Beckmans(4) have found that the amorphous phase is obtained at 10 at% zirconium in Zr-Co and Zr-Ni system. Independently, authors have also been successful in preparing amorphous alloys in the zirconium-poor corner of (Fe,Co,Ni)-Zr quaternary system by rapidly quenching their melts(5) and found that they exhibit interesting

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magnetic properties(6,7,8). In the present paper, we report on the formation range of amorphous phase in these systems and their characteristics such as thermal stability and mechanical properties.

II. Experimental

Mixtures of each pure metal were melted in argon atmosphere by using a high frequency furnace and the melt was solidified by sucking into a quartz tube having about 5 mm inner diameter. From these master alloys, continuous ribbon specimens were prepared in the form of about 0.5 mm width and about 0.015 mm thickness by using a single roller type spinning apparatus. The amount per run was about 2 g and the rotation speed of the steel roll with 200 mm diameter was of the order of 6000 rpm.

The amorphous nature of the as-quenched sample was examined both by X-ray diffraction method using Mo-K_{α} radiation and transmission electron microscopy. The crystallization temperature upon heating was measured in a differential thermal analyzer by heating at a rate of 8.33×10^{-2}°C/s. Hardness and fracture strength of the alloys were measured by a Vickers microhardness tester with a 50 g load and an Instron-type tensile testing machine at a strain rate of 1.7×10^{-3}/s. The ductile-brittle transition temperature was obtained for the specimens annealed for 6000s at various temperatures in evacuated silica capsule. The degree of ductility was evaluated from the radius of curvature at fracture in a simple bend test.

III. Results and Discussion

1. Formation range of amorphous phase.

It has been known that zirconium which is one of the early transition elements forms amorphous alloys by connecting with the later transition elements such as copper, nickel, cobalt and iron. Figures 1 to 3 show respective phase diagram of Ni-Zr, Co-Zr and Fe-Zr binary system and the composition range of amorphous alloys obtained by melt-quenching techniques. Most of amorphous alloys found in the past are located around deep eutectic compositions in zirconium-rich region. However, we have recently found that the amorphous single phase can be obtained in the limited composition range around a shallow eutectic at about 10 at% zirconium in three phase diagrams(5). These composition ranges are also shown in the figures. Figure 4 shows the X-ray diffraction data of $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys. Intensity curve of each alloy indicates that they are surely amorphous.

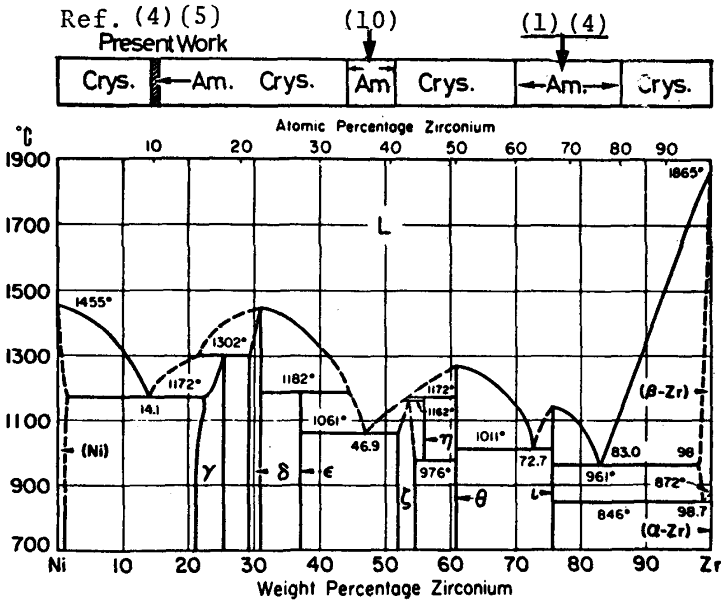

Fig. 1 Formation range of amorphous phase in Ni-Zr alloy system.

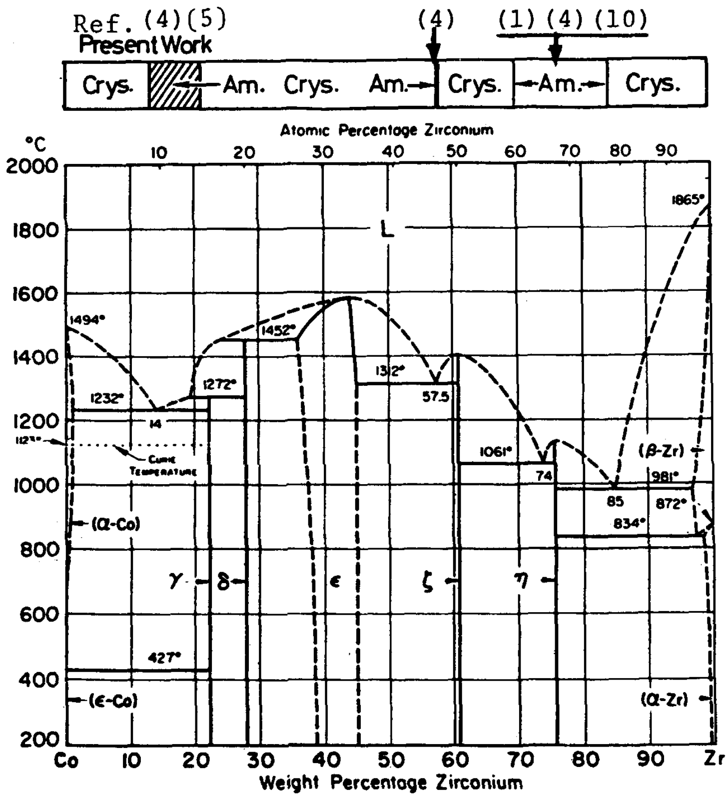

Fig. 2 Formation range of amorphous phase in Co-Zr alloy system.

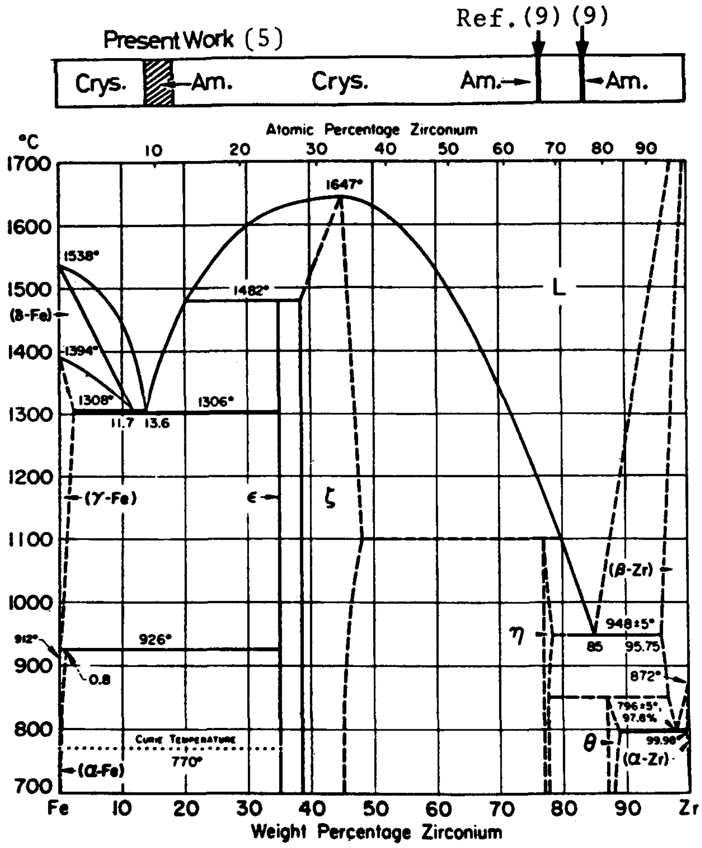

Fig. 3 Formation range of amorphous phase in Fe-Zr alloy system.

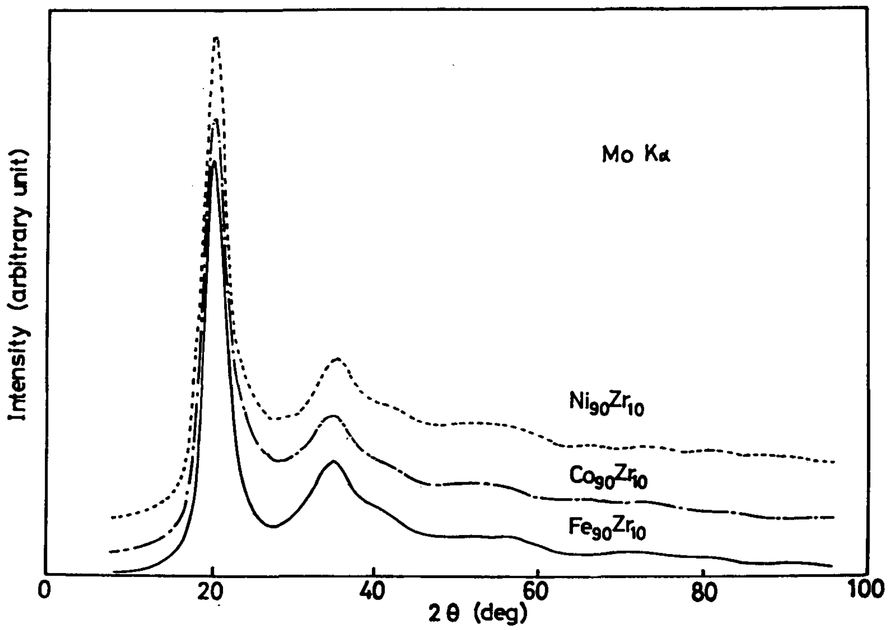

Fig. 4 X-ray diffraction intensity curves of $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$ adn $Ni_{90}Zr_{10}$ binary amorphous alloys.

In the present results there are two important findings. One is the fact that the amount of zirconium necessary for amorphous formation is extremely low in the present alloys. In generally, the amorphous alloys in metal-metal systems have been found almost invariably in the intermediate composition range where stable complex compounds are formed. Therefore, it is sure that the present data are new knowledges important to understand more extensively the amorphous structure and amorphous formation mechanism. The other is the fact that the present alloys contain a large quantity of ferromagnetic elements of iron, cobalt and nickel, compared with the other amorphous alloys found so far. Therefore one can expect that these amorphous alloys may be useful as soft-magnetic materials simillar to the metal-metalloid type amorphous alloys.

2. Thermal stability upon heating.

The thermal stability of amorphous structure is evaluated from the degree of crystallization temperature. Figure 5 illustrates the differential thermal analysis curves for $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$ and

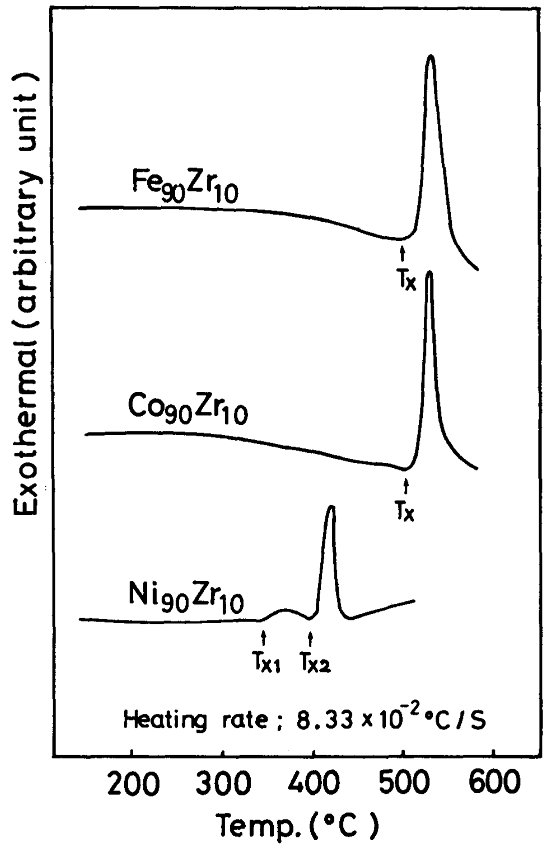

Fig. 5 Differential thermal analysis curves of $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ amorphous alloys.

$Ni_{90}Zr_{10}$ amorphous alloys. The former two alloys exhibit one sharp exothermic peak, whereas Ni-based alloy exhibits two peaks suggesting that crystallization takes place in two stages. Figure 6 shows the composition dependence of crystallization temperature in Fe-Co-Ni quasi-ternary system with 10 at% zirconium. As seen in the figure, the crystallization temperature Tx varies mainly depending on the nickel content and decreases with increasing nickel content. Judging from these data, the present amorphous alloys possess Tx comparable to the other metal-metalloid type amorphous alloys as seen in Table 1. As a result, it is said that the thermal stability of the present alloys are fairly high despite their low contents of amorphous-forming element.

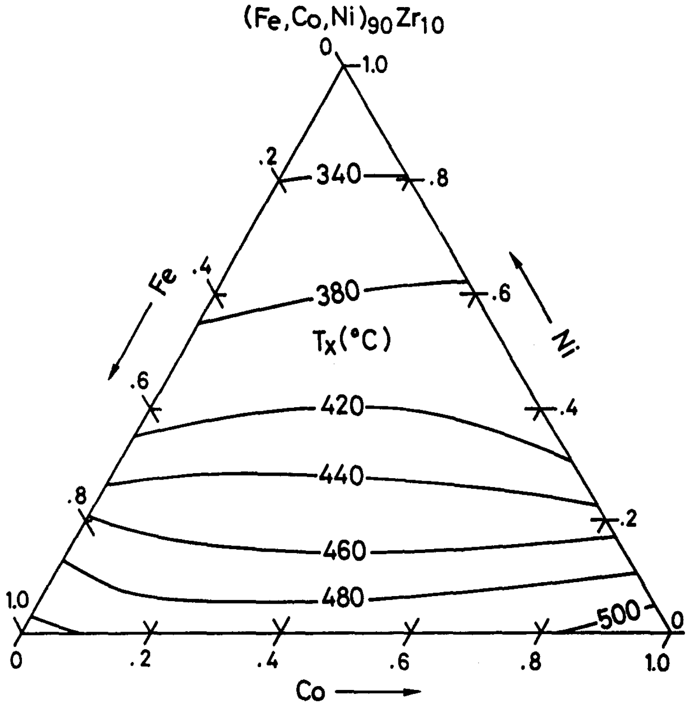

Fig. 6 Composition dependence of crystallization temperature in Fe-Co-Ni ternary system with 10 at% zirconium.

3. Mechanical properites

A number of studies have been made on the mechanical properties for metal-metalloid type amorphous alloys and it has been known that their hardness and strengths depend strongly on the alloy composition.[12] On the other hand, there are only a few data for metal-metal type amorphous alloys[13]. Therefore, mechanical properties of the Fe-Zr, Co-Zr and Ni-Zr amorphous alloys were examined. Figure 7 shows the change in hardness with zirconium content. The hardness value in all alloy systems increases with zirconium content and its level of each alloy system lowers in the order of iron, cobalt and nickel. Such a tendency in hardness coincides with the previous results[11] for the metal-metalloid type amorphous alloys. Also, tensile fracture strength of these alloys varies on the level of 1700-2100 MPa lower than the values of the metal-metalloid systems as shown in Table 1.

Tensile fracture occurs on the shear plane at about 54 degree to the tensile axis in the direction of thickness and the fracture surface consists of a smooth region by shear slip and a vein-like region by plastic instability, similar to general fracture morphology for many other amorphous alloys[12]. Furthermore, the present amorphous alloys possess a good bend ductility in the as-quenched state and can be bent through 180 degree over a razor without any cracks.

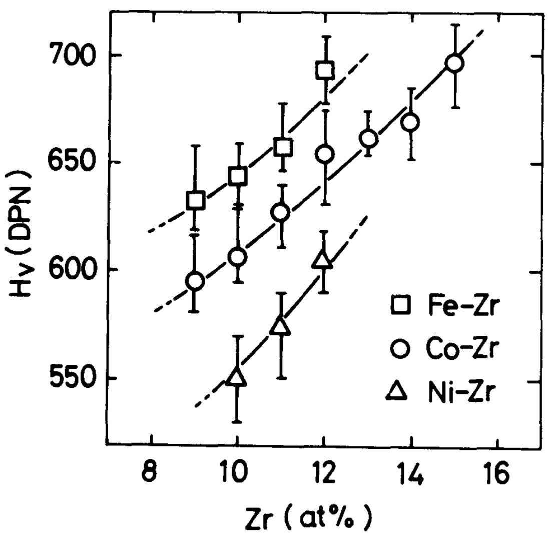

Fig. 7 Effect of zirconium on the hardness of Fe-Zr, Co-Zr and Ni-Zr binary amorphous alloys.

Ductile-brittle transition behavior was examined as functions of the aging time and temperature. As an example, a change in fracture strain during isochronal aging for 100 min is shown in Fig. 8, wherein the results of $Fe_{80}P_{13}C_7$ and $Fe_{78}Si_{10}B_{12}$ are also shown for comparison. The strain on the outer surface required for fracture, ε_f is estimated from the relation $\varepsilon_f = t/(2r-t)$, where r is the radius of curvature of bent sample at fracture and t is the thickness of the ribbon sample. The temperature for beginning of embrittlement, T_f is about 430°C for $Fe_{90}Zr_{10}$ alloy and is much higher than the values of $Fe_{80}P_{13}C_7$ and $Fe_{78}Si_{10}B_{12}$ alloys.

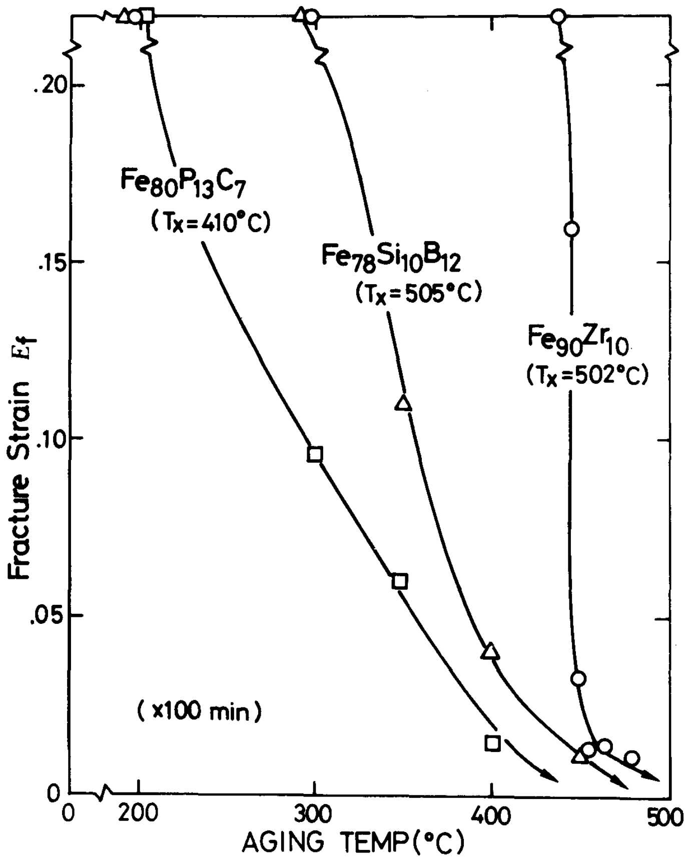

Fig. 8 Change in fracture strain of several amorphous alloys by isochronal aging for 100 min.

From comparison with the data of Tx, it is sure that the $Fe_{90}Zr_{10}$ alloy remains ductile until just before the crystallization onset. Such a high resistance against embrittlement by heating is in contrast to the previous results that the metalloid-bearing iron-based amorphous alloys exhibit T_f much lower that Tx.

As mentioned above, the (Fe,Co,Ni)-Zr amorphous alloys have various characteristics different from the metalloid-bearing amorphous alloys. Table 1 shows the comparison between the present metal-metal type alloys and the metal-metalloid type alloys in the values of Hv, σ_f, Tx and T_f.

IV. Conclusion

In the present work, new type of amorphous alloys was found in zirconium-poor side of (Fe,Co,Ni)-Zr quaternary system. Zirconium content in amorphous alloys was limited to 9-11 at% for Fe-Zr, 9-16 at% for Co-Zr and 10-11 at% for Ni-Zr system. Vickers hardness

and fracture strength of these binary alloys were about 550-700 DPN and 1700-2100 MPa, respectively. They also exhibited high crystallization temperatures and high embrittlement temperatures.
In particular the present iron-based amorphous alloys have high embrittlement temperatures compared with the metalloid-bearing iron-based amorphous alloys.

Table 1. Comparison of Vickers hardness(Hv), fracture strength (σf), crystallization temperature(Tx) and critical fractured temperature(Tf) between the present amorphous alloys and the metalloid-bearing amorphous alloys.

Alloy	Vickers hardness H_V (DPN)	Fracture strength σ_f (MPa)	Crystallization temperature (8.33×10^{-2} °C/s) T_{x_1}(°C)	T_{x_2}(°C)	Critical fractured temperature T_f(°C,x6ks)	T_f/T_x
$Fe_{91}Zr_9$	630	-	-	501	-	-
$Fe_{90}Zr_{10}$	640	2100	-	502	430	0.86
$Fe_{89}Zr_{11}$	660	-	-	497	-	-
$Co_{91}Zr_9$	590	-	-	506	-	-
$Co_{90}Zr_{10}$	600	1880	-	503	440	0.87
$Co_{89}Zr_{11}$	620	-	-	495	-	-
$Ni_{90}Zr_{10}$	550	1700	343	396	360	1.05
$Ni_{89}Zr_{11}$	570	-	341	390	-	-
$Fe_{80}P_{13}C_7$*	760	3000	410	-	290	0.71
$Fe_{78}Si_{10}B_{12}$*	910	3200	505	-	310	0.61
$Co_{75}Si_{15}B_{10}$*	910	2900	480	-	460	0.96
$Ni_{78}Si_{10}B_{12}$*	860	2400	464	-	430	0.93

* from Ref. (11)

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